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[54] **TANNING IMPROVEMENTS**

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[63] Continuation-in-part of Ser. No. 751,032, Aug. 8, 1968, abandoned.

[30] **Foreign Application Priority Data**

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[58] **Field of Search** 8/94.22, 94.23, 94.26, 8/94.24

[56] **References Cited**

UNITED STATES PATENTS

3,519,378	7/1970	Leverkusen et al.	8/94.26
3,391,557	12/1966	Neher et al.	8/94.22
3,102,772	9/1963	Robinson, Jr.	8/94.26
3,010,780	11/1961	Plapper et al.	8/94.26
2,950,950	8/1960	Plapper et al.	8/94.23
2,693,996	11/1954	Von Fuehs	8/94.27
2,178,874	11/1939	Harvey	8/94.26
1,800,574	4/1931	Thauss et al.	8/94.22

OTHER PUBLICATIONS

Progess in Leather Science 1920–1949, 1948 pages 520–525.

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[57] **ABSTRACT**

A process for tanning hides or skins comprises first treating the hides or skins with a basic salt of a multivalent metal; and then treating the hides or skins with a reaction medium containing a water-soluble salt of a dibasic organic acid, the water-soluble salt being one that forms an alkaline solution in water, and being present in an amount sufficient to maintain an alkaline pH in the reaction medium.

29 Claims, No Drawings

TANNING IMPROVEMENTS

This application is a continuation-in-part of my copending U.S. application Ser. No. 751,032, filed Aug. 8, 1968 and now abandoned.

This invention relates to the production of leather.

Traditionally hides and skins are tanned, after washing and treating with lime to remove any residual hair, with a basic salt of chromium or aluminum.

In the past, leather has been rendered waterproof by treatment with alkylated succinic and malonic acids and derivatives thereof. This process is conducted in an acid medium and results merely in an impregnation of the leather by the acids, and does not produce a chemical reaction between the leather and acid.

An object of this invention is to provide an improved process with which a leather having increased substance, improved flexibility, and outstanding waterproofing properties is produced.

The invention comprises a process for the tanning of hides or skins by treatment with a basic salt of a multivalent metal; and then in a reaction medium containing a water-soluble salt of a dibasic organic acid, the water-soluble salt being one that forms an alkaline solution in water, and being present in an amount sufficient to maintain an alkaline pH in the reaction medium. During treatment with the water-soluble salt, a reaction occurs between the water-soluble salt and the leather, resulting in the chemical bonding of dibasic organic acid residues to the leather.

Preferably after treatment with the basic salt of a multivalent metal the hide or skin is neutralized for example, with a weak alkali such as sodium bicarbonate or ammonia.

The process of the invention can be carried out on hides and skins that have been suitably prepared for tanning, for example by washing and treating with alkali, or on a hide or skin that has previously been tanned, for example, by a vegetable tanning process (vegetable tanned crust stock). Suitable hides and skins which can be treated by the process of the invention are, for example, bovine stock and sheep-skins.

Suitable basic salts of multivalent metals which can be used are any of the basic tanning salts of multivalent metal that are well known in the art and have been used as tanning agents, and include particularly basic salts of metals having a valency of three or more, e.g. chromium, aluminum, zirconium and cerium. Salts of mineral acids are usually preferred, especially sulphuric acid. Particularly good results have been obtained using basic chromium sulphate, which can for example be prepared by adding sodium carbonate to a solution of chromium sulphate or chrome alum.

The quantity of basic salt used is usually sufficient to give up to about 3.5 percent by weight (calculated as metal oxide) based on the weight of the leather. Particularly good results have been obtained using a quantity of basic salt sufficient to give from 1.5 to 3.0 percent by weight of metal oxide based on the weight of the leather.

The dibasic organic acid is preferably one having carboxyl groups separated by a chain containing seven or more carbon atoms and can be an aliphatic or aromatic dicarboxylic acid, especially a long chain aliphatic acid having between 7 and 36 carbon atoms, including, saturated dicarboxylic acids, e.g., azelaic acid, sebacic acid, straight chain C–12 and C–19 dicarboxylic acids and

di-oleic acid, and unsaturated dicarboxylic acids, e.g., di-linoleic acid. The presence of unsaturation in the aliphatic chain of an aliphatic carboxylic acid is found to give a leather having decreased flexibility but improved perspiration resistance. Increasing the length of the chain is often found to give improved flexibility, perspiration resistance and water-shedding properties.

The dibasic organic acid salt is a water-soluble salt having an alkaline reaction in water, and is preferably an alkali metal or ammonium salt, or a salt of an organic base such as an amine salt. Excellent results have been obtained using ammonium salts of dibasic organic acids.

The quantity of dibasic organic acid salt required to maintain the desired pH is usually not less than 1 percent by weight of the leather, particularly from 2 to 10 percent, e.g. 5 percent. In many instances, it has been found desirable to conduct the reaction of the leather with the dibasic organic acid salt in the presence of a water-soluble or water-miscible alcohol. Suitable alcohols include benzyl alcohol and cyclohexanol.

Also in accordance with this invention it has been found that an outstanding improvement in the properties of the treated leather can be obtained if after treatment with the dibasic organic acid salt the leather is further treated with a salt of a multivalent metal. This can be a basic salt, for example, the basic salt initially used or any other suitable basic salt, or a normal salt, for example a copper, zonc or nickel salt, particularly a sulphate. This after treatment contributes to a still further increase in substance, and confers hydrophobic properties on the final product. The quantity of basic or normal salt used is usually such as to give from 1.0 to 3.0 percent by weight (calculated as metal oxide) based on the weight of the leather.

The treatment of the hide or skin is preferably carried out by immersing the hide or skin in aqueous solutions of each of the reagents in turn for a time sufficient for reaction to occur. This is usually between 2 and 24 hours. If desired, the solutions can be agitated or stirred. The reactions usually proceed at an acceptable rate at room temperature, but if necessary elevated temperatures, for example up to about 50°C can be used. The hide is preferably washed with water and sammed after each stage of the treatment, and finally dried out.

After treatment by the process of the invention, the leather can be degreased, for example with a petroleum fraction, and subjected to any of the normal finishing operations, such as, for example, fat-liquoring and dyeing, although it is often found that the conventional fat-liquoring step can be omitted or at least substantially reduced in amount.

The invention is illustrated by the following examples.

EXAMPLE 1

This Example describes the production of a modified chrome leather using the process of the invention.

A tanned chrome leather is prepared by treatment of a hide or skin with a solution of basic chromium sulphate to a shrinkage temperature of 90° – 100°C. The leather is aged for 24 hours and freed from uncombined materials by washing.

The leather is then neutralized with sodium bicarbonate and treated with a 1 normal solution of sodium sebacate. The total amount of sebacate used is 10 percent

by weight of the shaved weight of the leather. After completion of the reaction, the stock is washed free from excess reactant and dried out to make a hydrophilic crust stock or treated with further basic chromium sulphate to produce a hydrophobic leather of high substance. It is found in subsequent processing of the leather that the conventional fat-liquoring step can often be omitted, or at least substantially reduced in amount.

EXAMPLE 2

This example describes the preparation of a further modified chrome leather using the process of the invention.

A tanned chrome leather is prepared by treating a hide or skin with a solution containing 33 percent by weight of the hide or skin of basic chromium sulphate (equivalent to 1.5 percent by weight Cr_2O_3), to a shrinkage temperature of 90° – 100°C. The leather is aged for 24 hours, washed free from uncombined salts and neutralized with 0.75 percent by weight of the leather of sodium bicarbonate. To the exhaust liquor is added 5 percent by weight of the leather of di-oleic acid in the form of its ammonium salt, and the leather is run with the liquor in a tanning drum to equilibrium. The treated leather is again washed free from uncombined salt and rechromed with 1.0 percent by weight of Cr_2O_3 in the form of a basic chromium sulphate (33 percent by weight) for 3 hours. After resting overnight, the leather is neutralized with sodium bicarbonate to bromocresol green, rinsed, dyed, lightly fat-liquored, set and dried out.

EXAMPLE 3

This example describes the preparation of another modified chrome leather using the process of the invention.

A hide or skin is chrome tanned as described in Example 2 and treated with 5 – 10 percent by weight of a straight chain C - 19 dicarboxylic acid salt in the presence of 3 – 5 percent by weight of benzyl alcohol of cyclohexanol. After this treatment, it is re-chromed and further treated as described Example 2.

What is claimed is:

1. A process for the tanning of a hide or skin comprising treating the hide or skin with a basic tanning salt of a multivalent metal; then chemically reacting the hide or skin with an aqueous medium containing a water-soluble salt of a dibasic organic acid, the water-soluble salt being one that forms an alkaline solution in water, and present in an amount sufficient to maintain an alkaline pH in the medium; and after treatment with the dibasic organic acid salt, further treating the leather with a salt of a multivalent metal.

2. A process according to claim **1,** in which the hide or skin is neutralized after treatment with the basic salt of a multivalent metal and prior to treatment with the salt of a dibasic organic acid.

3. A process according to claim **1,** in which the multivalent metal has a valence of three or more.

4. A process according to claim **3,** in which the multivalent metal is selected from the group consisting of chromium, aluminum, zirconium and cerium.

5. A process according to claim **1,** in which the basic salt of a multivalent metal is a mineral acid salt.

6. A process according to claim **1,** in which the quantity of basic salt used is sufficient to give from 1.5 to 3.0 percent by weight calculated as metal oxide based on the weight of the leather.

7. A process according to claim **1,** in which the dibasic organic acid is a dicarboxylic acid in which the carboxyl groups are separated by a chain having 7 or more carbon atoms.

8. A process according to claim **7,** in which the dibasic organic acid is one in which the carboxyl groups are separated by a chain containing from 7 to 36 carbon atoms.

9. A process according to claim **8,** in which the dibasic organic acid is a saturated dicarboxylic acid.

10. A process according to claim **9,** in which the dibasic organic acid is selected from the group consisting of azelaic acid, sebacic acid, a straight chain C-12 or C-19 dicarboxylic acid, and di-oleic acid.

11. A process according to claim **7,** in which the dibasic organic acid is an unsaturated dicarboxylic acid.

12. A process according to claim **11,** in which the unsaturated dibasic organic acid is di-linoleic acid.

13. A process according to claim **1,** in which the salt of the dibasic organic acid is selected from the group consisting of alkali metal salts, ammonium salts and salts of organic bases.

14. A process according to claim **1,** in which the quantity of dibasic organic acid salt used is from 2 to 10 percent by weight of the leather.

15. A process according to claim **1,** in which the further treatment with a salt of a multivalent metal is with a basic salt.

16. A process according to claim **15,** in which the further treatment with a basic salt is with the same basic salt as that initially used.

17. A process according to claim **1,** in which the further treatment with a salt of a multivalent metal is with a normal salt.

18. A process according to claim **17,** in which the normal salt is selected from the group consisting of copper, zinc and nickel salts.

19. A process according to claim **1,** in which the hide or skin is immersed in aqueous solutions of each of the reagents in turn.

20. A process according to claim **1,** that is carried out at a temperature of up to 50°C.

21. A process according to claim **1,** in which the hide or skin is washed with water after treatment with each of the reagents.

22. A hydrophobic leather tanned with a basic tanning salt of a multivalent metal compound and containing chemically bonded residues of a dibasic organic acid, said leather being produced by (a) treating a hide or skin with a basic tanning salt of a multivalent metal, (b) then chemically reacting the hide or skin with an aqueous medium containing a water-soluble salt of a dibasic organic acid, the water soluble salt being one that forms an alkaline solution in water, and present in an amount sufficient to maintain an alkaline pH in the medium, and (c) after treatment with the dibasic organic salt, further treating the hide or skin with a salt of a multivalent metal.

23. A leather according to claim **22,** in which the dibasic organic acid is an dicarboxylic acid in which the carboxyl groups are separated by a chain having 7 or more carbon atoms.

24. A leather according to claim **22,** in which the multivalent metal of the basic tanning salt is selected

from the group consisting of chromium, aluminum, zirconium and cerium.

25. A leather according to claim 22, in which the basic tanning salt of a multivalent metal is a mineral acid salt.

26. A leather according to claim 23, in which the dibasic organic acid is one in which the carboxyl groups are separated by a chain containing from 7 to 36 carbon atoms.

27. A leather according to claim 26, in which the dibasic organic acid is a saturated dicarboxylic acid.

28. A leather according to claim 27, in which the dibasic organic acid is selected from the group consisting of azelaic acid, sebacic acid, a straight chain C-12 or C-19 dicarboxylic acid, and di-oleic acid.

29. A leather according to claim 26, in which the dibasic organic acid is di-linoleic acid.

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